ORIGINAL PAPER

Composting as Sustainable Managing Option for Seaweed Blooms on Recreational Beaches

Engracia Madejón[1] · Marco Panettieri[2] · Paula Madejón[1] · Alfredo Pérez-de-Mora[3]

Abstract

Purpose Seaweed blooms are an irregular but frequent phenomenon in many coastal areas and during the touristic season, can cause limitations for recreational use of beaches. Here, we propose composting of seaweed removed from the shoreline as alternative to current management practices (e.g. disposal in landfills or incineration).

Methods A co-composting strategy with garden prune waste was chosen for the treatment of seaweed blooms removed from the beaches. Composting was performed in windrows of 10 m long, 1.5 m wide and 1 m high using different ratios of algae and garden prune residues (1:2; 1:1 and 2:1) at a composting facility in Rota (Cádiz, Spain).

Results Characteristic temperature profiles consisting of a very brief mesophilic phase, a 15–20-day thermophilic phase (maximum of 50–70 °C) and a second mesophilic phase (40–35ºC) after 30–50 days were observed. After curing for more than 160 days, a stabilized non-phytotoxic composted material (50–70 g kg^{-1} C; 2–3 g kg^{-1} N; C/N ratio of 21–27 and electrical conductivity between 1.8–2.4 mS cm^{-1}) was obtained. Composting worked best using a 2:1 ratio (prune waste:algae). The composted organic material showed larger presence of stabilized lignin-derived compounds as assessed via nuclear magnetic resonance. No odors were detected during the composting process suggesting that open-air treatment is feasible.

Conclusion The co-composting strategy provides a safe, local and sustainable approach to deal with seaweed blooms during peaks of recreational use and in situations where algae have to be removed.

Graphic Abstract
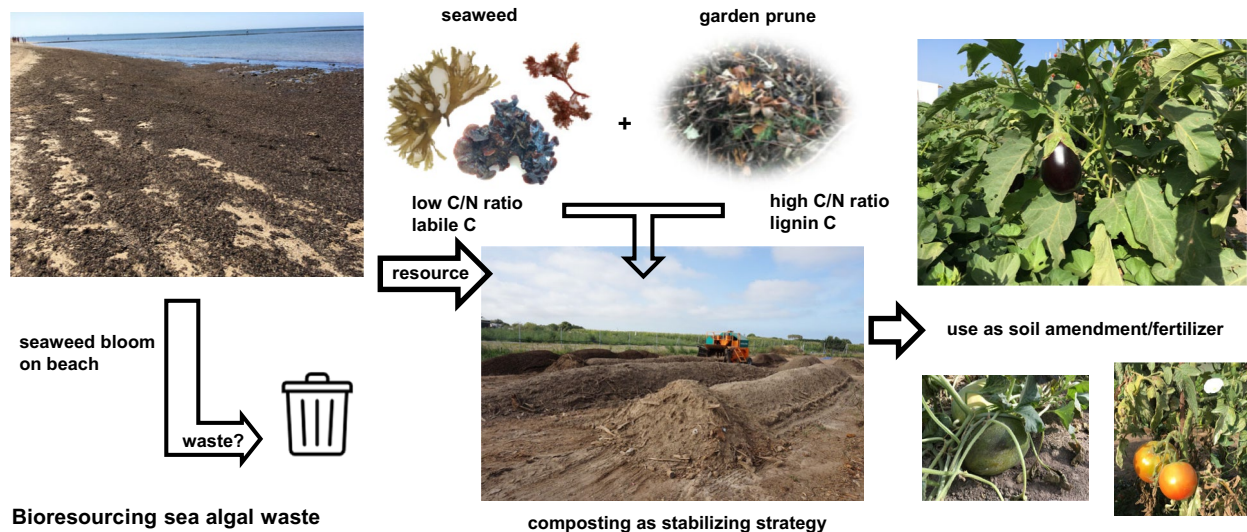
Extended author information available on the last page of the article

Statement of Novelty

Composting offers an attractive option to stabilize and bio resource algae waste accumulated on the shoreline following seaweed blooms. Excess of algae debris on recreational beaches poses a significant management dilemma for coastal municipalities worldwide. In contrast to other substrates, composting of algae has been marginally explored. As a result, data from pilot composting demonstrations at larger scale are lacking. An additional challenge not addressed yet in previous reports is that mechanical removal by the coastal cleaning services can incorporate substantial amounts of sand to the algae, that is difficult to remove when tons of material have to be processed. Our composting approach provides an easily-implementable yet robust strategy to alternatively process and revalue locally excess of algae waste.

Introduction

Seaweed play a vital function in coastal systems in terms of habitat for marine organisms and natural protection against erosion [1, 2]. Deposition of plant debris on the shoreline is also crucial for the ecology of coastal areas including aspects such as: (i) food and habitat for small crustaceans and other species, which then provide food for fish, crabs, and nesting and migrating birds, (ii) seed and plant distribution as well as (iii) sand traps that stabilize the coastal line [1]. Nonetheless, excessive accumulation of macroalgae on the shoreline, both autochthonous and invasive, as a result of seaweed blooms can negatively affect water quality, ecological balance and recreational use of beaches [3]. This is particularly troublesome during the touristic season as seaweed rapidly decay under warm temperatures, produce odors and/or attract flies and their larvae. This has ultimately negative consequences for tourism and other economic aspects of the impacted municipalities (e.g. commercial fisheries, waterfront property value and waste management) [4, 5]. Due to the irregular nature of such incidents and the extent of biomass that can accumulate on the beach, municipalities are faced with the challenge of handling tons of seaweed material in a matter of a few hours.

Generally, the algae are removed mechanically by the municipal cleaning services and finally disposed of in landfills or incinerated [6]. Other potential options include processing in bioplants or composting with municipal domestic waste in large treatment plants, but such facilities may not be present locally and require acceptance by plant managers. In addition, the potential to bioresource the treated seaweed material locally is lost.

Direct application of seaweed as nutrient source for agriculture was and is still a traditional practice in some coastal areas [7–9]. Popular experience agreed that harvested seaweed could be a good fertilizer for improving vegetable cropping as long as it was handled properly [10]. The application of non-stabilized residues to soil may result in fermentation of the substrate added causing odors, production of toxic metabolites for plants as well as leaching of N and undesired substances to groundwater. Other problems that may arise depend on the nature and characteristics of the products applied and include changes in soil pH, salinity and/or the accumulation of heavy metals in the soil [11].

Composting is a robust and sustainable option for stabilizing a wide variety of organic residues [12, 13]. Seaweeds are not only a source of macro- and micronutrients (e.g., Mg, Sr, B and Fe), but also contain amino acids, vitamins as well as plant-growth promoting substances including cytokines, auxins, and abscisic acid [14]. These characteristics make seaweed biomass an attractive resource for composting. However, the high moisture content and relatively low C/N ratio of seaweed generally favor rapid material decomposition and N losses [7]. The potential high salinity of marine algae further complicates composting of this material [14]. Thus, to produce optimal composting conditions for sea algae it is necessary to combine it with a complementary substrate such as garden prune waste with higher C/N ratio, higher lignocellulose content and better bulking properties that allow air to flow and circulate better [9, 15]. The presence of lignin-derived compounds in compost improves C sequestration in soil and the formation of humus [16]. Solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR) is one of the most powerful techniques to assess chemical changes in the decomposition and quality of natural organic matter [17]. As C atoms from different functional groups resonate in specific spectral areas, the relative abundance of biomolecules in a sample can be identified via ^{13}C-NMR [18]. In this manner, changes in the relative contribution of easily degradable molecules (e.g. carbohydrates and proteins) in the fresh material versus more chemically stabilized molecules (e.g. lignin-derived compounds and lipids) in the mature compost and, thus, the efficiency of the composting process can be assessed [19].

In the present work we investigated the potential of co-composting macroalgae at pilot scale to obtain a stabilized product that can be safely applied as soil amendment for agriculture or restoration of derelict soils, particularly in semiarid areas with low organic content. The ultimate goal was to develop an optimal composting process that: (i) can be easily adopted by coastal municipalities facing seaweed blooms, (ii) that can be implemented at small local composting facilities, and (iii) that represents a realistic and economically-sound alternative to current waste management practices.

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We hypothesized that co-composting of seaweed with garden prune waste results in a stabilized composted material that can be used as soil amendment. This hypothesis fits with the Green Deal objectives [20] and the new Circular Economy Action Plan [21]. In the core of these documents, EU waste policy aims to contribute to the circular economy by extracting high-quality resources from waste. In this sense seaweed retired from the recreational beaches could be transformed to a valuable fertilizer helping to the transition to a modern, resource-efficient and competitive agriculture. The composting process was monitored by means of temperature, moisture, total-C, total-N, N-ammonium and N-nitrate concentrations. Micronutrients and heavy metals were further assessed in the original materials as well as the end products. Phytotoxicity and odor emissions were also controlled during the composting process. In addition, changes in the chemical structure of the composted materials were assessed via nuclear magnetic resonance.

Materials and Methods

Study Area

Collection of seaweed material was performed under permission of the municipality of Rota (Cádiz, Southern Spain). The affected coastline known as "Playa de la Costilla" is about 4 km long (Figure S1). The municipality of Rota is characterized by a hot summer Mediterranean climate (Csa according to the Köppen climate classification) with a yearly annual temperature of 17.8 °C and an average cumulative precipitation of 588 mm. Seaweed accumulations on Rota's beach as well as on other parts of the coast of Cádiz are generally caused by the easterly wind known as "Levante" that blows westward and is particularly strong (3–5 of the Beaufort scale, occasionally up to 8) downwind of the Strait of Gibraltar. The "Levante" can be observed at irregular intervals, every two to three weeks with a duration of three to five days, throughout the year, but is most prominent between May and October.

Raw Materials

Sea algal waste (AW) material was collected mechanically from the beach using excavator shovels with the help of the municipality cleaning services in May 2019. The material was immediately transported to the composting plant "Compost Ecológico" located in the same municipality approx. 5 km away from the beach. The biomass collected was composed by macroalgae typically found on the intertidal region of the western coast of Cádiz. No invasive seaweed was identified in the material collected. Some of the species that could be identified during the sampling include

a variety of red, brown and green algae [22]: (i) red algae *Halopithys incurva* (Hudson) Batters, *Halymenia floresii* (Clemente y Rubio) C. Agardh, *Laurencia obtusa* (Hudson) J.V. Lamouroux, *Plocamium cartilagineum* (Linnaeus) P.S. Dixon, *Sphaerococcus coronopifolius* Stackhouse, (ii) brown algae *Halopteris scoparia* (Linnaeus) Sauvageu and *Padina pavonica* (Linnaeus) Thivy, and (iii) green algae *Codium decorticatum* (Woodward) M.A. Howe and *Codium tomentosum* Stackhouse.

Garden prune waste (GP) for co-composting was provided by the composting facility "Compost Ecológico". A physical and chemical characterization of the two raw "compostable" materials was carried out (Table 1). According to the Spanish and European Legislation seaweed collected from the beach may be considered as biodegradable/organic municipal waste, although there is no truly appropriate subcategory, whereas garden prune waste falls within the subcategory 200, 201 municipal waste from parks and gardens [23].

Composting Process

Composting was performed in windrow piles owing to the simple operation, low-cost and potential for scaling-up. The size of the windrows was approx. 15 m long, 1.5 m wide

Table 1 Chemical composition of the raw materials

Parameter	Units	Sea algal waste	Garden prune
Moisture	%	67.9 (6.93)	12.3 (0.93)
pH		7.98 (0.15)	8.07 (0.05)
EC	mS cm^{-1}	1.79 (0.10)	1.87 (0.28)
TOC	g kg^{-1}	155 (22.1)	508 (5.10)
N	g kg^{-1}	6.70 (0.80)	9.50 (0.80)
C/N		23.1	53.4
P_2O_5	g kg^{-1}	1.10 (0.20)	2.10 (0.90)
K_2O	g kg^{-1}	5.70 (2.90)	9.30 (1.60)
CaO	g kg^{-1}	89.3 (14.1)	18.6 (3.60)
MgO	g kg^{-1}	8.30 (1.30)	3.50 (0.40)
Na	g kg^{-1}	24.2 (2.10)	2.00 (0.60)
SO_3	g kg^{-1}	23.2 (5.30)	4.60 (0.20)
Fe	mg kg^{-1}	3711 (510)	377 (0.02)
As	mg kg^{-1}	6.38 (0.48)	4.96 (19.7)
Cd	mg kg^{-1}	< 0.01	< 0.01
Co	mg kg^{-1}	2.11 (0.61)	< 0.01
Cr	mg kg^{-1}	7.53 (1.04)	3.33 (0.14)
Cu	mg kg^{-1}	7.35 (2.03)	4.52 (0.75)
Mn	mg kg^{-1}	257 (61.0)	20.5 (3.80)
Ni	mg kg^{-1}	3.76 (0.85)	1.53 (0.07)
Pb	mg kg^{-1}	5.22 (2.29)	1.38 (0.40)
Zn	mg kg^{-1}	21.5 (3.19)	18.9 (2.26)

Mean values and standard deviation of true replicates (in brackets) of the measured variables N = 3

Fig. 1 Experimental design of the three windrows in the composting facility

Fig. 2 Image of a turning and a watering event in the pile

and 1 m high (Fig. 1). These measures were chosen to allow a better turning operation using the machinery available at the composting plant (Möschle Compost Turner). Building of piles was performed between the 2nd and 3rd of July 2019. Water was gradually added onto each windrow to avoid leaching and to reach an initial moisture content of about 40%. Aeration was achieved by mechanical turning and natural convection (Fig. 2).

Garden prune waste was crushed mechanically to obtain a final particle size of approx. 5–10 cm (80% on wet volume basis) and 20% of material with particle size > 10 cm. Seaweed material was neither pre-washed to remove sand attached to it nor cut prior to incorporation into the windrows. The sand content in the algae material was estimated to account for approx. 30% of the total wet volume. Co-composting of raw materials was performed using different ratios

of AW/GP waste depending on their physical and chemical characteristics. Three different windrows were built with the following composition on a volume basis: windrow 1 was a mixture of one part of AW and two parts of GP (1:2), windrow 2 was a mixture of one part of AW and one part of GP (1:1) and windrow 3 was a mixture of two parts of AW and one part of GP (2:1) (Fig. 1).

Piles were regularly watered to maintain an adequate moisture content. A total of 6 turning events at 1, 9, 15, 31, 47 and 72 days after windrows establishment were performed. Sieving to a particle size ≤ 15 mm of the final products was performed at 122 days.

Control of Parameters "In Situ" During Composting Process

The temperature profile was recorded as mean of six replicate measurements in each windrow using a digital thermometer equipped with a 1 m long probe (Crison, Thermometer 638 pt). The probe was inserted in 6 positions per pile and temperature readings were performed at 30 and 60 cm depth. At the beginning of the composting process temperature was recorded every 2–3 days for the first 2 weeks, subsequent measures were performed after each turning event, and at different times during the maturation phase.

Odor control was performed using a portable and programmable field olfactometer (Nasal Ranger®) that automatically creates a series of discrete dilutions by mixing the odorous ambient air with clean air (odour-free) depurated by the use of active carbon filters placed on one side of the device. For odor measurements panelists were placed at approx. 2–3 m distance from windrows and several air dilutions were created using the olfactometer. In this manner the optimum "Dilution-to-Threshold" (D/T) ratio was determined, i.e. the number of dilutions needed to make the odorous ambient air "non-detectable". Control measurements were made at 1, 31, and 72 days after windrow construction.

Compost Sampling and Analysis

Samples for physico-chemical analysis were collected at different times during the composting process. For each windrow and timepoint, three composite samples of approx. 10 L were collected from three different sections of the windrow at 10–40 cm depth. Composite samples resulted from mixing of 10 aliquots (1 L each).

Moisture content was measured gravimetrically by drying at 105 °C to constant weight. The pH and the electrical conductivity (EC) were measured in water-compost extracts 1:5 (w/v). Total organic matter (OM) was measured by loss ignition at 430 °C to constant weight. Kjeldahl N determination was performed according to Hesse [24].

Nitrate was extracted in water (1:5 w/v) and quantified in the aqueous extracts by a continuous flow auto-analyzer Luebbe GmbH AA3 dual channel (Norderstedt, Germany). Results were expressed as $N-NO_3^-$. Ammonium was extracted in KCl 2 M (1:5 w/v) and determined using the same flow auto-analyzer. Results were expressed as $N-NH_4^+$.

Mineral nutrients and trace element contents were determined after *aqua regia* digestion in a microwave oven by ICP-OES (CEN, 2002). Compost samples from the WEPAL programs [25] were also analyzed for quality control of analytical procedures. The results obtained for these samples diverged $\pm 5\%$ at maximum from the certified results.

Samples taken at different times of the composting process were subjected to phytotoxicity tests. A germination test with cress (*Lepidium sativum* L.) was performed in Petri dishes using water extracts from the compost. Control extracts consisted of deionized water [26]. Seed germination and root length were measured after 24 h and 72 h in both treatments (compost extracts and controls). The germination rate (G), the root length index (RLI) and the germination Index (GI) were calculated according to Tiquia and Tam [27].

Chemical Characterization of the Organic Matter Using Solid-State ^{13}C Nuclear Magnetic Resonance

Samples collected 1, 15, and 72 days after the establishment of the 3 windrows were analysed by ^{13}C Cross Polarization Magic Angle Spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy to assess the chemical changes of the organic matter from the raw material to the mature composted products.

The spectra were acquired on a Bruker Advance III HD 400 MHz widebore spectrometer operating at a ^{13}C frequency of 100.64 MHz. Samples were placed into ZrO_2 rotors of 4 mm OD with Kel-F caps spinning at 14 kHz at the magic angle.

Tetramethylsilane ($=0$ ppm) and glycine (176.04 ppm) were used to calibrate the ^{13}C chemical shifts. According to Knicker et al. [28], pulse delays were longer (500 ms) for the samples collected during the first sampling, since crystalline cellulose from undecomposed plant debris has longer relaxation times that could affect spectra acquisition (Figure S2). For successive sampling pulse delay was set to 300 ms, and 10,000 to 20,000 scans were acquired for each spectrum, depending on the C contents of the sample.

Spectra were divided into seven regions: alkyl-C (0–45 ppm), N-alkyl/methoxyl C (45–60 ppm), O-alkyl C (60–90 ppm), anomeric C (90–110 ppm), aryl C (110–140 ppm), heteroaromatic C (140–160 ppm), carboxyl/amide C (160–220 ppm) [18, 29]. NMR data were treated with the software MestReNova version 12.0.4–220 (© 2018

Mestrelab Research S.L.). Further information about peak assignments to biomolecules is reported in Table S1.

Results and Discussion

Monitoring of the Composting Process

Temperature

The temperature trend presented in Fig. 3a was obtained based on the average values given by the thermal probe at six different locations of the windrow at 30 and 60 cm depth. Ambient temperature is also depicted. The three windrows showed a brief initial mesophilic phase of a few hours during which temperatures of 35–55 °C were reached. This initial phase is generally associated with the metabolization of sugars and other readily-degradable organic sources.
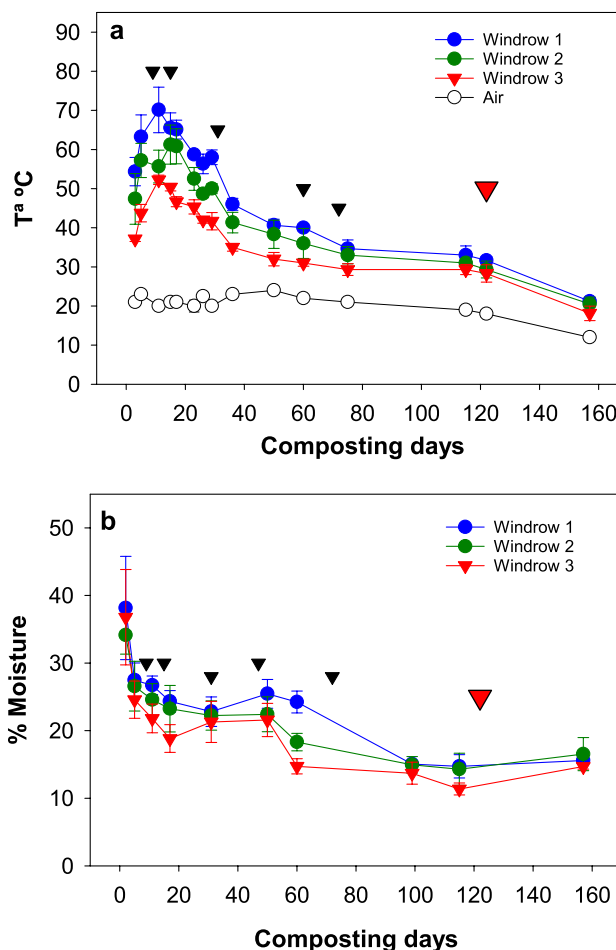
Fig. 3 Changes in the mean values of temperature (**a**) and moisture content (**b**) in the three windrows during the composting process. Bars indicate standard deviations. Black arrows indicate turning events. Red arrow indicates sieving event. (Color figure online)

The initial mesophilic phase was followed by a thermophilic phase of approx. 30 days for windrows 1, 23 days for windrow 2 and 15 days for windrow 3. During this phase, typically, cellulose and other more resistant materials are decomposed. The maximum temperature was reached after two turning events (days 9 and 15) and differed significantly between windrows with peaks at 70 °C for windrow 1, 62 °C for windrow 2 and 53 °C for windrow 3. The thermophilic phase was followed by a second mesophilic phase characterized by an initial temperature drop of approx. 15–20 °C until day 50 and a more gradual temperature decrease from 30–40 °C to approx. 20 °C (maturation or curing stage). Turning events on days 31, 47 and 72 did not result in any appreciable temperature increase. In previous works at laboratory [30, 31] and at pilot scale [32] similar temperature profiles were reported for co-composting AW with other types of organic mulching co-substrates.

It should be noted that for windrow 3, the pile temperature barely reached 55 °C, which is considered the threshold for the elimination of unwanted pathogens and seeds. The exposure time and temperature to inactivate relevant pathogens for windrow composting should be at least one to two weeks at 55 °C according to Böhm [33], although regulatory guidelines may differ for each country [34, 35]

Moisture

The initial moisture content of the two substrates was significantly different, being relatively large (67%) for AW and low (12%) for GP. Mixing of the substrates in the piles resulted in an initial intermediate moisture of the composting windrows around 35%. Changes in moisture content are depicted in Fig. 3b. Despite the intense watering procedures carried out during each turning event (Fig. 2), i.e. between two moisture measurements, and the continuous superficial watering performed during this active thermophilic phase, the moisture content of the three windrows showed a decreasing trend from an initial content of approx. 35% to 25–20% associated with the increase in windrow temperature. From day 20 to day 50, as temperature cooled down from the thermophilic maximum to 42–32 °C the moisture content remained relatively constant between 25 and 20%. During the final gradual temperature drop from day 50 to day 160 moisture gradually decreased to a final value of 15% for all windrows.

Haug [36] recommended optimal composting moisture content between 40 and 60% during the thermophilic phase for microbial activity. Other authors have reported that microbial activity may be inhibited when moisture content falls below 25% [37]. Maintaining humidity in the piles within the range mentioned above, particularly for windrow 3, was difficult likely as a result of the sand present that limited water retention. Nonetheless, temperature evolution for

windrows 1 and 2 as well as dynamics of other parameters explained below indicated adequate composting progress.

pH and Electrical Conductivity

pH measurements are useful to follow-up the different phases of the composting process and to assess the maturity of the resulting material (Fig. 4a). The pH of the material in the windrows ranged between 7 and 8 units during the 157 days of composting.

A drop in pH of 0.5 units was observed during the first 11 days, which could correspond to the release of short-chain acids resulting from the metabolization of sugars and readily decomposable materials. Following the initial pH drop, an increase of up to one pH unit was observed during the thermophilic phase from day 11 to day 31. This increase in pH is typically described as the result of the mineralization of acidic compounds, such as carboxylic and phenolic
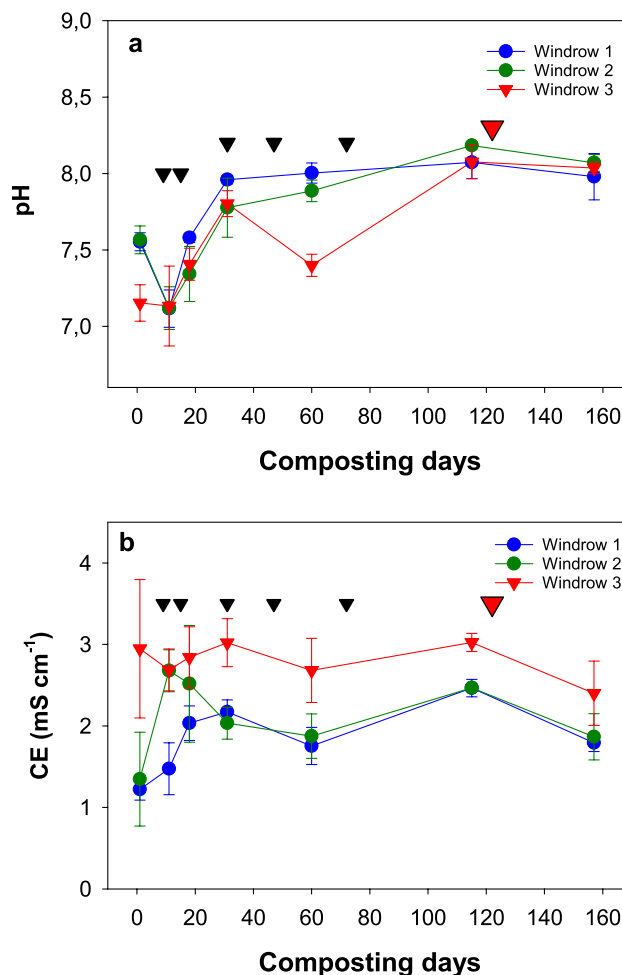
Fig. 4 Changes in the mean values of pH (**a**) and EC (**b**) in samples of the three windrows during the composting process. Bars indicate standard deviations. Black arrows indicate turning events. Red arrow indicates sieving event. (Color figure online)

groups, as well as the decomposition of amino acids and peptides with the consequent release of ammonium ions [38, 39]. During the second mesophilic and maturation phase pH values remained relatively constant at 8 for the three piles over time with the exception of a temporary drop to 7.5 at day 60 for windrow 3. The general trends for the pH indicate a good quality of the composted material obtained. Final values of pH are slightly alkaline (around 8) for all windrows and, thus, safe for plant health and agricultural use.

Salinity was of particular concern for both the development of the composting process as well as for the quality of the final product obtained. High salinity may cause osmotic stress, negatively affect microbial populations involved in the composting process and limit plant growth and/or productivity when high salinity compost is used as amendment. Salinity of the composting process was assessed by means of the electrical conductivity (Fig. 4b). The greater ratio of algae (two parts) to prune waste material (one part) resulted in average higher electrical conductivity (0.5–1 mS cm^{-1}) in windrow 3 compared to windrows 1 and 2. With the exception of the initial 11 days of composting, during which EC values dropped for windrow 3 and increased for windrows 1 and 2, the EC remained relatively stable for the rest of the incubation. Final EC values between 2.3 mS cm^{-1} for windrow 3 and 1.8 mS cm^{-1} for windrows 1 and 2 were reached at the end of the incubation. The EC values measured are well-below the threshold of 8 mS cm^{-1} for microbial cells lysis [40]. Since reduction in growth for sensitive plants may begin at an electrical conductivity in soil above 2 mS cm^{-1}, the composted materials obtained do not pose a risk in terms of salinity for agricultural use, as confirmed by the germination test reported in Section "Phytotoxicity of the Compost and Odor Nuisances" below.

Total Organic Carbon and Total Nitrogen

Figure 5 shows the evolution of TOC (Fig. 5a) and total N (Fig. 5b), respectively. Both the TOC and the N content of the windrows was strongly influenced by the ratio of prune waste and sea algae used, being highest for windrow 1, with a 1:2 ratio of algae to prune waste, intermediate for windrow 2 (1:1 ratio) and lowest for windrow 3 (2:1 ratio).

It should be noted that changes for both TOC and N contents were observed for all windrows during the thermophilic phase: TOC content showed a generalized decrease of approx. 5%, whereas different trends were recorded for N. For windrow 1 an increase of the N content was observed, windrow 2 maintained constant N levels and windrow 3 showed a decrease in N content (Fig. 5b). The decoupling of C and N dynamics is mainly due to the stoichiometric needs of composting microorganisms during the decomposition of organic matter and it can both result in enrichment or losses of N [36].
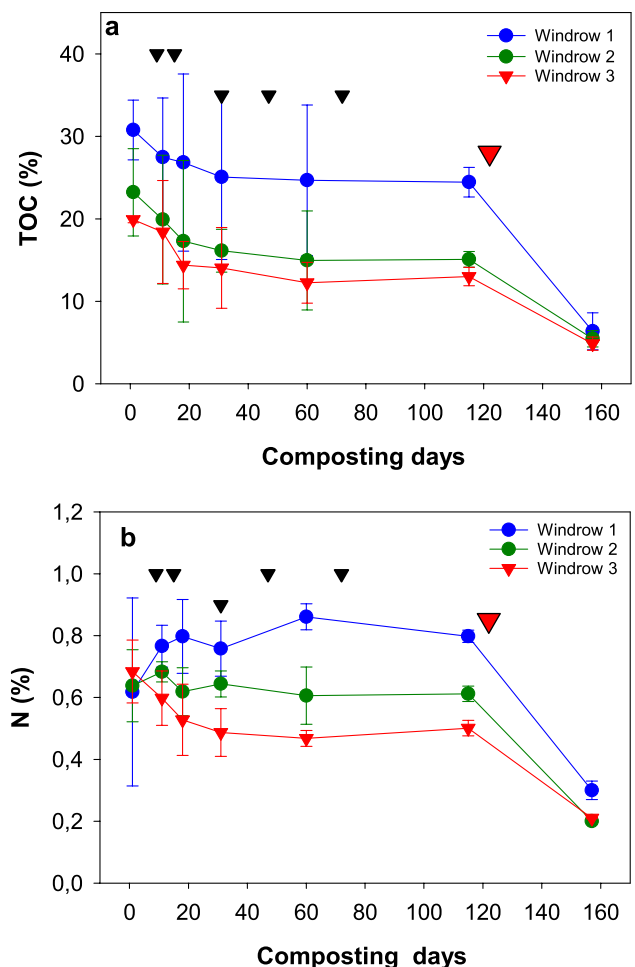
Fig. 5 Changes in the mean values of total organic carbon (TOC) (**a**) and N (**b**) in samples of the three windrows during the composting process. Bars indicate standard deviations. Black arrows indicate turning events. Red arrow indicates sieving event. (Color figure online)

During the second mesophilic stage, both TOC and N contents remained relatively stable with ranges between 270 g kg^{-1} TOC and 8 g kg^{-1} N for windrow 1, 170 g kg^{-1} TOC and 6.5 g kg^{-1} N for windrow 2 and 150 g kg^{-1} TOC and 5 g kg^{-1} N for windrow 3. The stabilization of both C and N contents is typically observed in the transition from raw material to mature compost [41, 42]. Losses of organic carbon observed during the composting (from day 1 to day 115) were 29, 22 and 18% for windrow 1, 2 and 3 respectively. Losses of organic matter between 20–30% have been reported by other authors in composting processes of other organic waste [42, 43]. Last sampling was performed after 157 days, after the sieving procedure using a 15 mm mesh sieve. Sieved material showed an expected significant drop in TOC and N contents consequent to the

removal of the coarse non-composted pruning particles, which have been reported to be richer in C and N [44].

Ammonium and Nitrate Contents

The initial average N-NH$_4^+$ concentration was larger for windrow 3 (15 mg kg^{-1}), with the highest proportion of algae; whereas similar ammonium levels were measured for windrows 1 and 2 (12–13 mg kg^{-1}; Fig. 6a). During the thermophilic phase, a generalized decrease in N-NH$_4^+$ concentrations was observed for all windrows and particularly for windrow 3, with an absolute decrease from 22 to 7 mg N-NH$_4^+$ kg^{-1}. This can be attributed to greater formation and loss of ammonia gas during this period as a result of the intense breakdown of organic matter and elevated temperatures within the piles [43, 45].

Between day 30 and day 60 a generalized increase in N-NH$_4^+$ concentrations was observed for all windrows (Fig. 6a). This is likely due to the onset of ammonification processes as the temperature cooled off between 15–20 °C in all windrows during the second mesophilic phase. As temperatures around 30 °C were reached in the piles, a second gradual decrease in N-NH$_4^+$ concentrations and a concomitant increase in N-NO$_3^-$ were observed (Fig. 6b). As nitrifying microorganisms perform best between 20 and 30 °C, nitrification processes thrived in detriment of ammonification processes once their optimum growth temperature range was reached [43, 45]. For windrow 3, nitrification was largest between days 30 and 60 with a net change in N-NO$_3^-$ from 15 to 60 mg N-NO$_3^-$ kg^{-1}. For windrows 2 and 1 an increase in N-NO$_3^-$ concentrations and, thus, in nitrification, was first observed after day 60 with a maximum content of 40 mg kg^{-1} on day 115 for windrow 2 and 25 mg N-NO$_3^-$ kg^{-1} on day 157 for windrow 1. The content of any of the inorganic forms of nitrogen in the materials is of great importance to determine its quality [46]. In the final products, the concentration of N-NH$_4^+$ was much lower than concentration of N-NO$_3^-$ which is related to the stabilization of organic matter. According to Bernal et al. [47] a N-NH$_4^+$/N-NO$_3^-$ratio lower than 0.16 indicated no phytotoxic effects. In our case the three products obtained presented ratio values lower than this index.

The greater N-dynamics and total N-NO$_3^-$ content for windrow 3 compared to windrows 2 and 1 at the end of the curing phase (day 157) are in line with the initial proportion of algae biomass in the windrows (windrow 3 > windrow 2 > windrow 1) and C:N ratios (windrow 3 < windrow 2 < windrow 1).

Quality of Final Composted Product

Organic Matter Quality

The NMR spectra reported in Figure S3 were divided into seven spectral regions following the assignments reported in Table S1. Relative contributions for each region (Table 2) highlighted increasing intensity in the region of O-alkyl C (60–110 ppm) with the increased proportion of algae biomass in the windrow (windrow 3 > windrow 2 > windrow 1). O-alkyl C is typically found in carbohydrate-derived compounds considered as fresh and easily available fraction of the organic matter [18, 29]. This higher contribution in carbohydrate-derived compounds found for the algae fraction was compensated by a lower contribution of methoxyl C (45–60 ppm). This region is assigned to lignin-derived compounds from plant material or to N-alkyl compounds derived from proteins in soils or material with high microbial proliferation [48]. According to the O-aryl C region (140–160 ppm) in which heteroaromatic C from lignin resonates, most of the methoxyl C signal can be assigned to lignin-derived material [49]. Therefore, AW showed a higher
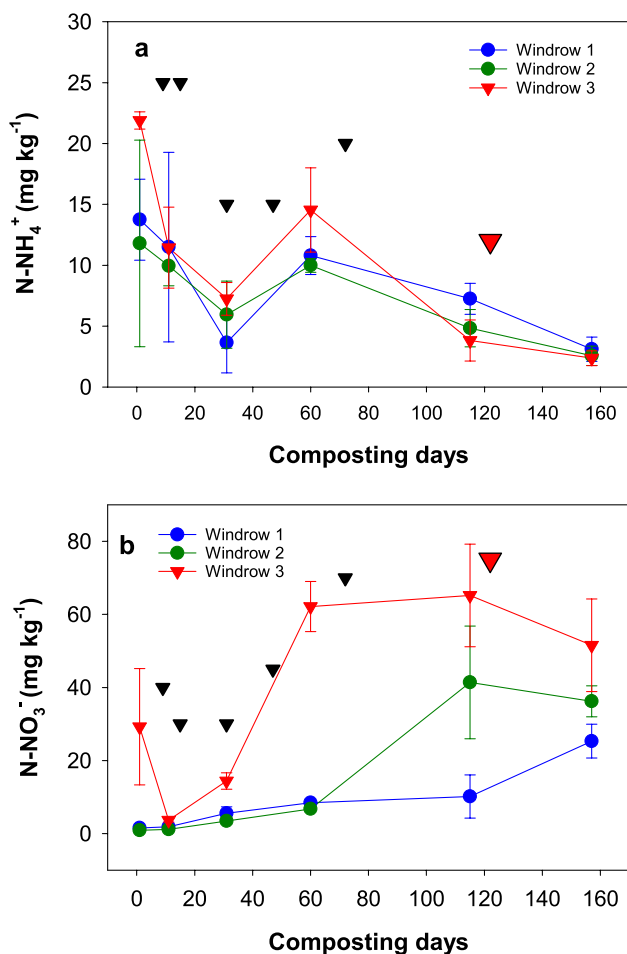

Fig. 6 Changes in the mean values of ammonium (**a**) and nitrate (**b**) in samples of the three windrows during the composting process. Bars indicate standard deviations. Black arrows indicate turning events. Red arrow indicates sieving event. (Color figure online)

Table 2 Integration values expressed as relative contribution of the seven spectral regions of ^{13}C NMR spectra for the three windrows at the three different sampling times. Spinning side bands not included

Spectral region	Windrow 1			Windrow 2			Windrow 3		
	Day 1	Day 15	Day 72	Day 1	Day 15	Day 72	Day 1	Day 15	Day 72
Alkyl	25.43	22.75	23.09	22.71	24.42	24.65	20.71	21.25	23.68
N-alkyl	10.41	11.76	11.23	10.64	11.35	11.70	11.00	10.34	10.65
O-alkyl	30.60	30.61	27.00	30.94	32.24	25.37	34.50	31.75	30.85
Anomeric	9.59	10.39	9.39	10.27	10.24	9.67	11.25	10.92	11.04
Aromatic	10.25	11.62	12.92	11.64	10.82	13.36	11.14	11.14	11.08
Heteroaromatic O$_5$	4.85	5.03	5.87	5.33	4.40	5.63	5.36	5.45	5.46
Carboxyl O	5.21	4.49	6.07	4.81	4.53	6.12	4.54	5.22	4.88
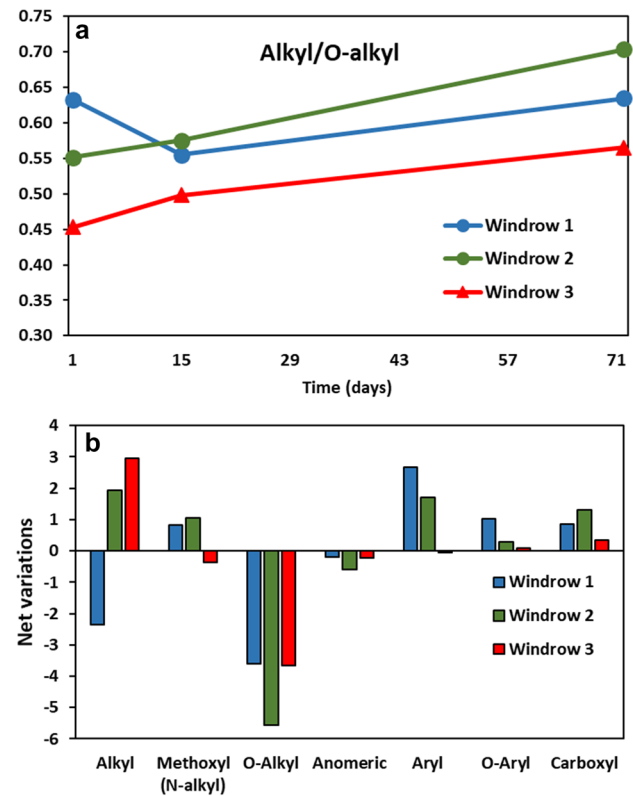
Fig. 7 a The alkyl to *O*-alkyl ratios calculated for the three windrows along the composting process. For this calculation, *O*-alkyl values included the anomeric C region. **b** Net variations of the relative contribution of each spectral region for the three windrows at the beginning and at the end of the composting process

relative contribution of O-alkyl signal (i.e. carbohydrates) and a lower contribution of heteroaromatic C (i.e. lignin) compared to garden pruning (Table 2).

As decomposition of carbohydrate-rich fresh material during the initial mesophilic and thermophilic phase progressed, microbial proliferation increased resulting in an enrichment of low-degradable lipid from undecomposed plant material (e.g. cutins and/or suberins) and microbial-derived lipids (e.g. membrane lipids or aliphatic chains from amino acids), resonating in the Alkyl-C region [50]. As a result of the different composition of AW and GP materials, lower Alkyl/O-alkyl ratios were observed at the beginning of the composting process for windrow 3 compared to windrow 2 and, in turn, to windrow 1 (Fig. 7a). Alkyl/O-alkyl ratio is a common index of organic matter stability [50], indeed the ratios calculated for all the windrows increased as the composted biomass matured (Fig. 7a). For windrow 2 and 3 a net increase of 17 and 26%, respectively, was observed for the Alkyl-C/O-alkyl ratio. For windrow 1, the greater contribution of GP material likely caused an initial decrease of the Alkyl/O-alkyl ratio at day 15. This can be related to

the lower microbial proliferation in this windrow and to the decomposition of freely available lipids such as fatty acids and alcohols of plant origin, leading to a decrease of Alkyl C contribution (Fig. 7b).

The net variations along the composting process of the relative intensities for each spectra region showed that the decrease in O-alkyl contribution was observed for all the windrows (Fig. 7b). These losses were compensated by increases in the contribution of the aryl, heteroaromatic, methoxyl and carboxyl C regions for the windrows 1 and 2. Considering the assignments reported in Table S1, higher contributions from these regions indicate an enrichment in OM compounds more resistant to degradation, such as lignin and other aromatic structures. For windrow 3 and, to a lesser extent windrow 2, the decrease of O-alkyl signal was compensated by an increase of Alkyl-C signal, a proxy of higher microbial proliferation that was not observed for windrow 1.

These results further support the co-composting approach selected. The large amounts of labile and nutrient-rich organic matter from AW (i.e. O-alkyl signal assigned to carbohydrates) rapidly triggered microbial activity. However, this easily-degradable organic matter had to be compensated with the external addition of lignin-rich material from GP to ensure the curing of the composted material within reasonable time and obtain a more stabilized material at the end of the process [51, 52].

Phytotoxicity of the Compost and Odor Nuisances

The values for germination percentage (%G) and germination index (GI) during composting of the three windrows was included in supplementary materials (Table S2). The %G values for the materials of the three windrows were similar or even higher than those found for the control test from the first week. Therefore, phytotoxicity disappeared already after the first week of composting in the three windrows resulting in GI values higher than 100 and well above the phytotoxicity threshold of 60. Other studies have demonstrated that high GI values can be reached for algae-based compost material. Indeed, Castaldi and Melis [53] and Cocozza et al. [54] observed that most of the tested GI values were higher than 100, which indicates that the compost can stimulate plant growth without causing phytotoxic effects.

The results of olfactometric measurements performed after the turning events did not offer any odor nuisances during the process (data not shown). Even at a very low dilution with the Nasal Ranger, no odors were appreciable at a 2–3 m distance of the piles. The nature of the material (plant and seaweed derived), the adequate frequency of turning events as well as appropriate composting operation prevented the development of odor nuisances during the composting process.

Table 3 Final characterization of the three composts obtained. Mean values and standard deviation for different sampling locations within the same windrow (in brackets) of the measured variables N = 3

Parameter	Unit	Windrow 1	Windrow 2	Windrow 3
pH		7.98 (0.15)	8.07 (0.05)	8.03 (0.03)
EC	mS cm^{-1}	1.79 (0.10)	1.87 (0.28)	2.40 (0.39)
TOC	g kg^{-1}	63.7 (24.2)	54.7 (9.80)	48.7 (12.9)
N	g kg^{-1}	3.00 (0.30)	2.01 (0.02)	2.10 (0.20)
C/N		21.2	27.3	23.2
P$_2$O$_5$	g kg^{-1}	1.20 (0.20)	0.90 (0.10)	0.90 (0.40)
K$_2$O	g kg^{-1}	3.40 (0.60)	2.50 (0.30)	2.70 (0.90)
CaO	g kg^{-1}	96.6 (42.0)	91.5 (0.20)	103 (3.90)
MgO	g kg^{-1}	5.30 (0.70)	4.60 (0.50)	5.50 (0.70)
Na	g kg^{-1}	1.90 (0.10)	1.80 (0.20)	2.30 (0.20)
SO$_3$	g kg^{-1}	3.10 (0.30)	2.50 (0.20)	2.90 (0.50)
Fe	mg kg^{-1}	4400 (660)	3900 (200)	3900 (60)
As	mg kg^{-1}	6.38 (0.48)	4.96 (1.07)	4.36 (2.73)
Cd	mg kg^{-1}	0.04 (0.03)	0.02 (0.02)	0.02 (0.05)
Co	mg kg^{-1}	1.91 (0.53)	1.56 (0.16)	1.69 (0.35)
Cr	mg kg^{-1}	11.4 (8.47)	6.53 (1.34)	7.91 (3.04)
Cu	mg kg^{-1}	12.1 (6.56)	12.4 (6.97)	7.84 (4.24)
Mn	mg kg^{-1}	166 (22.0)	149 (18.2)	172 (20.2)
Ni	mg kg^{-1}	6.13 (3.47)	3.55 (0.12)	4.13 (1.63)
Pb	mg kg^{-1}	7.04 (4.32)	6.20 (4.73)	4.43 (2.90)
Zn	mg kg^{-1}	28.1 (11.4)	20.1 (5.58)	21.4 (6.30)

Chemical Characterization of the Final Products

Sieving (≤ 15 mm) was performed after the maturation phase and the final product of each windrow was characterized (Table 3). Alkaline pH and low EC were observed for all the three products; both the salinity and the phytotoxicity values were below the corresponding thresholds for sensitive plants [55]. It should be noted that the TOC (~ 5%) and N (~ 0.25%) values were much lower than those obtained before sieving, since the thick pruning fraction represents a large C and N pool that is commonly removed from the final product during this step [44]. Similarly, the content of P (~ 0.1%) and K (~ 0.3%) in the stabilized products was moderate, whereas the content of Mg (~ 0.5%) and Ca (~ 10%) was relatively high compared to previously reported algae co-composted material [15]. The material discarded in the screening, rich in N and C, will be used in the plant as bulking agent for the composting of new batches of algae or other materials (e.g. horse manure).

The content of both metals and metalloids (Table 3) was in general lower than that typically found in biosolid and municipal waste compost [56, 57] and below the threshold established by the Spanish and European legislation for farming substrates. Although algae may bioaccumulate metals and metalloids [58], the original raw material collected

had very low content of these elements (Table 1). Similar results have been reported for composts obtained from marine algae [6, 15, 54].

According to the Spanish Legislation [21] the product obtained can be classified within group 5 "mixed substrates for farming" as vegetal earth, that is, a product obtained from mixing of sand and organic products (e.g. composted material) with a final organic matter content between 3 and 15%. The nutritional value of the stabilized product may be improved if less sand is removed together with the algae during collection on the beach. However, this may require other type of machinery for removal that may not be available at many municipalities. To the best of our knowledge this is the first work that reports on composting of seaweed removed by the regular practice of the coastal cleaning services and not selectively collected for composting experiments.

Implications for Resource Management and Future Perspectives

The accumulation of seaweed on the coast, known in Spanish as "ribazones" or "arribazones" is a common phenomenon in many areas of the world that generally coincides with stronger winds and sea roughness (e.g. the Monsoon in Asia) [7]. The algae are torn from the seabed and end up in piles on the beach. During typical bloom events in the study area seaweed can accumulate up to biomass densities of 2.5 kg m^{-2} (dry weight), that is, around 7.5 kg m^{-2} (wet weight) or even more over various kilometers of coastal line. Under such circumstances, seaweed management may be deemed necessary. Heavy machinery is usually employed for removal, resulting in a substantial amount of sand removed together with the algae. This makes management of seaweed even more challenging for municipalities since the material collected may not be appropriate for other uses, e.g. biogas production, landfills or thermal treatment. In the context of this project the application of the excess sand for top dressing of "greens" in a local golf course is under evaluation. Alternatively, the sand may be returned to the beach for ecological restoration purposes.

It should be noted that for this study sand was removed by a digger machine from the coastal service. The use of other type of machinery such as track screeners may improve mechanical removal of seaweed by dragging less sand to minimize their impact on the coastal ecosystem. This will, in turn, improve the composting process and the quality of the final product. It is important to outline that removal activities should be conducted only when seaweed washed ashore become a problem.

The co-composting approach presented here is safe, demands little infrastructure and is implementable in small composting facilities. This allows for local bioresourcing

of the algae waste thereby improving the C-footprint and sustainability of the overall process [59].

Conclusions

Algal waste is a natural substrate rich in easily degradable compounds such as carbohydrates and proteins that can be revalorized as stabilized soil amendment by co-composting with substrates rich in lignin compounds such as garden prune waste. For co-composting of algae mixtures with ratios of algae:co-substrate between 1:2 and 1:1 are recommended to achieve temperatures above 55 °C during the thermophilic phase that prevent proliferation of pathogens.

Co-composting of seaweed with garden prune waste does not generate odor nuisances and, thus, can be performed outdoors in the absence of exhaust systems. The resulting composted materials is non-phytotoxic and, thus, can be used as soil amendment for agriculture or restoration of derelict land.

Substantial amounts of sand may be removed together with the algae depending on the machinery used by the coastal cleaning services and the ability of the operators. Sand associated with the algae can limit the composting process by negatively affecting temperature dynamics, the moisture of the composting pile as well as the organic matter content and quality of the final product.

Author Contributions Based on the CASRAI's CRediT definitions of contributor roles, the authors contributed to this work as follow: Conceptualization: APDM, EM. Data curation: APDM, MP, PM, EM. Formal analysis: MP, PM, EM. Funding acquisition: APDM, EM. Investigation: MP, PM, EM. Methodology: APDM, MP, PM, EM. Project administration: APDM, EM. Resources: PM, EM. Software: APDM, MP, PM. Supervision: APDM, EM. Validation: MP, PM, EM. Visualization: MP, PM. Writing – original draft: APDM, MP. Writing – review & editing: PM, EM. Engracia Madejón (EM), Marco Panettieri (MP), Paula Madejón (PM), Alfredo Perez de Mora (APDM).

Data availability The data that support the findings of this study and of the TAUW 201905_5 project "Bioresourcing sea-algal waste" are available from the corresponding and lead authors, upon reasonable request.

Code availability The code is available from the corresponding and lead authors, upon reasonable request.

Declarations

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Authors and Affiliations

Engracia Madejón[1] [ORCID] · **Marco Panettieri[2]** · **Paula Madejón[1]** · **Alfredo Pérez-de-Mora[3]**

✉ Engracia Madejón
  emadejon@irnase.csic.es

[1] Instituto de Recursos Naturales Y Agrobiología de Sevilla, Avenida de Reina Mercedes, 10 41012 Sevilla, Spain

[2] Instituto de Ciencias Agrarias (ICA-CSIC), c/Serrano 115-B, 28006 Madrid, Spain

[3] Department of Soil and Groundwater, TAUW GmbH, Landsbergerstrasse 404, 81241 Munich, Germany